Gasification of Iowa Coal in the SYNTHANE PDU Gasifier

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Introduction

Vast deposits of high sulfur caking coals found in the eastern and midwestern United States can be converted to clean gaseous energy by gasification. In the 1980's many coal gasification plants are expected to be constructed in the United States to produce a high-Btu gas as a supplement to the dwindling supply of natural gas. One important consideration in the development of a coal gasification process is the acceptability of various coal feedstocks. The SYNTHANE process is one such process for the manufacture of high-Btu gas from coal. This report demonstrates the capability of using the SYNTHANE process for the gasification of the mildly caking high sulfur coal from Iowa. This coal is not only present in substantial reserves (7.2×10^9 tons) (1) but is also convenient to the large energy markets of the Midwest. The Iowa coal for this study is from the Iowa Coal Project Demonstration Mine #1 of Iowa State University. This coal bed is located in the southwest corner of Mahaska County and is part of the Cherokee Group.

Experimental Equipment

A schematic flow diagram of the SYNTHANE PDU gasification system is shown in figure 1. This system combines the steps of fluidized-bed pretreatment, free-fall carbonization and fluidized-bed gasification. The pretreater is an 8-foot long, 3/4-inch diameter pipe with a 2-1/2-foot long, 1-inch diameter expanded zone. Both sections of pipe are schedule 80 and made of 304 stainless steel. The pretreater is enclosed by four individually controlled heaters that supply heat for startup and to counter radiation losses. The carbonizer is a 6-foot long, 10-inch diameter schedule 40 pipe made of 304 stainless steel located directly above the gasifier. Electric heaters surrounding the carbonizer maintain the temperature at 1000° F. The gasifier is a 6-foot long, 4-inch diameter schedule 40 pipe made of 310 stainless steel. Surrounding the gasifier is a 10-inch schedule 40 pipe made of 304 stainless steel which acts as a pressure shell. In the annulus three individually controlled electric heaters, wrapped in a 2-inch thick blanket of insulation, supply heat for startup and to counter radiation loss during operation. A 1/8-inch pipe entering the base of the gasifier serves as the gas distributor. A thermowell made of 3/8-inch pipe located in the center of the gasifier extends from 1-inch above the gas distributor to the top of the carbonizer. Twelve thermocouples inserted into the thermowell detect internal temperatures from the base of the gasifier to the top of the carbonizer. A variable speed extractor screw located at the base of the gasifier maintains the bed height by removing reacted char. The raw product gas leaving the top of the gasifier is filtered to remove fine particles and cooled in a series of two water-jacketed condensers. Effluent water and tar are collected in a receiver. The dry gas is then analyzed by mass spectrometric and chromatographic methods prior to metering the flow rate.

Experimental Procedure

The caking Iowa coal (analysis shown in table 1) was crushed and sized to an average size of 240 microns with a U.S. Standard mesh range of 20 X 0. The pulverized coal was fed to the base of the pretreater under pressure (40 atm) at a rate of about 20 lb/hr. The coal then moved through the pretreater in a fluidized state with nitrogen

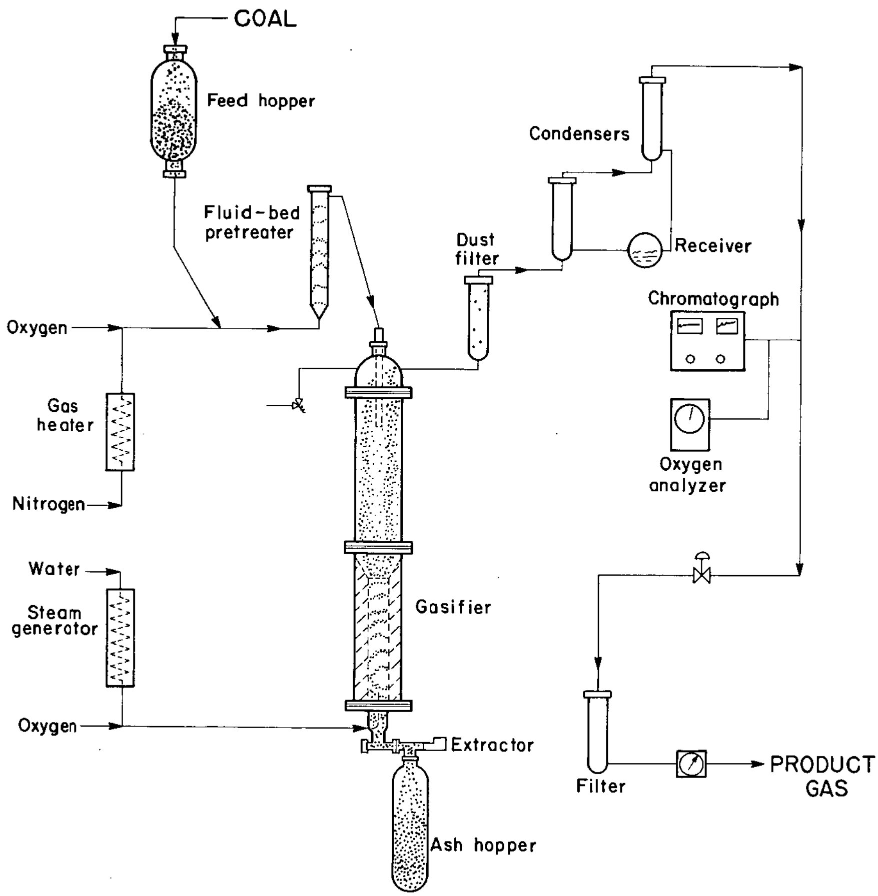

Figure 1 - SYNTHANE PDU GASIFIER.

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and oxygen. The pretreating conditions were the same as those developed for the pretreatment of Illinois No. 6 coal as reported by Gasior (2). The decaked coal emptied from the top of the pretreater and was gravity fed into the gasifier through the carbonizer, countercurrent to the exiting product gas. A mixture of steam and oxygen entering the base of the gasifier provided both the reactant and fluidizing gases. Gasifier temperatures were maintained by varying the flow rate of oxygen to the reactor. A fluidized-bed height of about 68 inches was maintained by adjusting the char extraction rate to coincide with the coal feed and gasification rates.

Discussion and Results

The operating conditions and results for the three experimental gasification tests are shown in table 2. Coal feed rates for these tests ranged from 17.6 to 19.9 lb/hr, which are equivalent to coal throughputs of 37.4 to 42.4 lb/hr ft^3 of gasifier volume. Average gas inputs of 0.35 lb oxygen/lb coal and 1.8 lb steam/lb coal resulted in a superficial gas velocity of 0.29 ft/sec at 40 atmospheres pressure in the 4-inch gasifier. No difficulty was experienced in maintaining temperature control in the fluidized-bed with the average of the maximum gasifier temperatures ranging from 1761° to 1832° F, and no slag-sintering problems occurred at peak gasifier temperatures of 1850° F.

The results of the three tests showed that carbon conversions ranged from 77.0 to 80.2 percent and steam conversions or decomposition ranged from 14.3 to 16.9 percent. Raw gas analysis showed that the hydrogen sulfide yield was 0.77 SCF/lb coal, maf, for the 8 percent sulfur coal, while product gas yields (H_2 + CO + CH_4 + C_2H_6) averaged 13.6 SCF/lb coal, maf, with equivalent methane yields (CH_4 + C_2H_6) ranging from 3.45 to 3.60 SCF/lb coal, maf.

Comparing test results using Iowa coal to similar test results using Illinois No. 6 coal, as reported by Forney (3), the Iowa coal results showed higher carbon conversions (78.6 vs. 71.8 percent), lower product gas yields (13.6 vs 14.9 SCF/lb coal, maf) and higher hydrogen sulfide yields (0.77 vs. 0.36 SCF/lb coal, maf). The higher temperature accounted for the high carbon conversion while the high sulfur content of the coal resulted in high hydrogen sulfide yields and slightly lower hydrogen yields. The high steam to coal ratio (1.8/1) resulted in a high hydrogen to carbon monoxide ratio (3.3/1). Calculations indicate that shift equilibrium for all tests is achieved between the average temperature and the temperature at the top of the bed. The high hydrogen to carbon monoxide ratio would eliminate the need for a shift reactor and can be controlled to give the desired ratio for methanation ($\sim$3.05/1) by adjusting the steam to coal ratio.

Table 3 shows the distribution of sulfur forms in the coal and char. Sulfur forms are determined by extraction of the coal and char samples with hydrochloric and nitric acids. The analysis and a weight balance between the coal fed and char produced indicates that most of the sulfur in the coal is converted to hydrogen sulfide and trace sulfur compounds in the gas and tar. About 0.7 weight percent of the sulfate sulfur, 0.3 weight percent of pyritic sulfur and 26.9 percent of the organic sulfur found in the coal remain in the char after gasification. Pyritic sulfur is easily removed by its reaction with hydrogen.(4) The sulfate sulfur is also converted to hydrogen sulfide.

As shown in table 4, there are a number of trace sulfur compounds in addition to the large quantities of hydrogen, carbon monoxide, carbon dioxide, methane, ethane and hydrogen sulfide produced in the gasifier. These trace compounds are separated from the product gas by cryogenic distillation and by measured mass spectrometric analysis. The product gas contains 3.2 volume percent sulfur compounds and would require a sulfur clean up prior to methanation.

The analysis and fusibility of ash for Iowa coal and char are shown in table 5. Certain compounds contained in the ash of coals undoubtedly contribute to the carbon conversion, gasification rates, the quantity and the quality of gas produced. (2, 5, 6) According to Grossman (7) and Ely (8) iron is the major contributor in lowering the fusion temperature of coal ash under reducing conditions. Gasior (2) also found that coals having the greatest percentage of calcium and magnesium compounds have the lowest sintering temperature. Results of these Iowa coal gasification tests appear to confirm these findings since no sintering was observed.

The major effluent problem associated with the steam-oxygen gasification of Iowa coal is the unreacted steam leaving the gásifier as contaminated water condensate. The analysis of this water is shown in table 6 along with a coke plant water analysis for comparison. The amounts of the contaminants vary greatly, but the cyanide and thiocyanate content of the gasification effluent is much smaller than in the coke plant effluent while the phenol and COD content are greater. It is believed that the high steam partial pressure in the SYNTHANE gasifier causes conversion of nitrogen compounds to ammonia. Coke plant water pollution has been alleviated to some extent (9), but some problems still remain. The Iowa coal effluent water analysis shows no significant difference from other reported analyses of SYNTHANE effluent waters. (10)

A coal tar byproduct is also produced from the gasification of Iowa coal. This tar leaves the gasifier as a vapor with the unreacted steam and is easily separated from the effluent water condensate by decanting. The tar is heavier than water and negligible amounts of a lighter-than-water phase are produced. Table 7 shows the analysis and physical properties of the tar produced. For the gasification of Iowa coal, tar yields averaged 7.3 percent of the coal fed, compared to 4.0 percent for Illinois No. 6 coal. Gasior (2) and Nakles (11) have found that feeding the coal below the top of the fluidized-bed can significantly reduce the tar yield. A simulated ASTM distillation of this tar shows that less than 50 percent of the tar boils below 940° F. The high percentage of sulfur (3.2%), however, could drastically limit the direct use of these tars as a fuel. With an effective desulfurization process, the desulfurized tar could be used as a nonpolluting boiler fuel or an oil refinery feedstock.

Conclusions

Overall results from an exploratory study to gasify a mildly caking, high sulfur Iowa coal in the SYNTHANE PDU gasifier have shown that carbon conversions of 80 percent and steam conversions of 16 percent can be achieved at average maximum gasifier temperatures of 1832° F and coal throughputs of 40 lb/hr ft^3. These results confirm published findings that coals having the largest amount of calcium and magnesium compounds have the lowest sintering temperatures and that the amount of sulfur in the tar and gaseous products is generally related to the amount of sulfur in the coal. The effluent water shows no significant difference from other SYNTHANE gasifier condensates, and is generally similar to coke-oven byproduct water.

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Table 1. - Analysis and free-swelling index of Iowa coal

Class	High-Volatile C
Analysis (as received), %	
Moisture	2.9
Volatile Matter	36.2
Fixed carbon	41.2
Ash	19.7
Hydrogen	4.4
Carbon	59.2
Nitrogen	0.8
Oxygen	8.0
Sulfur	7.9
Free-swelling index	1.5

Table 2. - Operating conditions and results for Iowa coal gasification tests in a fluidized-bed at 40 atmospheres pressure

Test No.	209	210	211
Operating time, hrs.	6.0	6.0	6.0
Coal feed rate, lb/hr	17.6	19.5	19.9
lb/hr ft^3 gasifier	37.4	67.0	68.0
Bed height, in.	68.4	67.9	68.0
Steam rate, lb/hr	35.3	35.1	35.3
Oxygen rate, SCFH	75.5	81.5	76.9
Temperature, °F			
peak	1844	1850	1850
average maximum	1761	1832	1832
average	1664	1691	1702
top of bed	1572	1576	1601
Superficial gas velocity at avg. max. temp., ft/sec	0.28	0.29	0.29
Yields and conversions			
Carbon conversion, weight percent	80.2	77.0	78.6
Steam decomposition, weight percent	14.3	15.4	16.9
Product gas 1/ yield, SCF/lb coal, maf	13.7	13.5	13.6
Equivalent methane 2/ yield, SCF/lb coal, maf	3.60	3.53	3.45
Tar yield, % of coal 3/ fed	7.6	7.0	7.4
Product gas analysis, dry, N_2 free (%)			
H_2	33.6	33.2	33.7
CO	9.2	10.3	10.7
CH_4	11.9	12.1	11.9
CO_2	40.7	39.8	39.1
C_2H_6	1.4	1.4	1.4
H_2S	3.2	3.2	3.2

1/ $H_2 + CO + CH_4 + C_2H_6$.

2/ $CH_4 + C_2H_6$.

3/ As received after air drying.

Table 3. - Distribution of sulfur forms in Iowa coal and char and the sulfur conversion

	Sulfate	Pyritic	Organic
% S in Coal	0.41	5.18	2.35
% S in Char	0.01	0.05	2.55
lb char/lb coal	0.29	0.28	0.26
% Converted	99.3	99.7	73.1

Table 4. - Trace components in dry product gas[1/] from the fluidized-bed gasification of Iowa coal with steam and oxygen at 40 atmospheres pressure

Test No.	209	210
Hydrogen Sulfide	11,040	12,000
Carbonyl sulfide	250	250
Methyl mercaptan	<5	<5
Thiophene	<5	<5
Sulfur dioxide	-	-
Benzene	100	N.D.[2/]
Toluene	100	N.D.[2/]
Xylene	-	-

1/All values in ppm by volume.
2/Not determined.

Table 5. - Analysis and fusibility of ash[1/] of Iowa coal and char

Major Elements in Ash	Coal, %	Char, %
SiO_2	35.4	34.1
Al_2O_3	14.0	14.7
Fe_2O_3	39.5	44.0
TiO_2	0.8	0.6
CaO	3.6	2.8
MgO	0.4	0.3
Na_2O	1.3	0.4
K_2O	0.9	0.7
SO_3	1.5	0.1
Fusibility of ash, °F		
Initial deformation temp.	1900	1930
Softening temperature	1950	1980
Fluid temperature	2040	2030

1/Staff, Office Director of Coal Research Methods of Analyzing and Testing Coke and Coal, BuMines Bull. 638, 1967, 82 pp.

Table 6. - Effluent water analysis[1] from the fluidized-bed gasification of Iowa coal with steam and oxygen at 40 atmospheres pressure[2]

Test No.	209	210	211	Coke Plant
pH	9.0	9.2	9.1	9.0
Suspended solids	6	16	15	50
Phenol	2060	2340	2180	2000
COD	14500	17400	16800	7000
TOC	4600	4970	4850	N.D.[3]
Thiocyanate	108	129	135	1000
Cyanide	0.029	0.027	0.122	100
Chloride	22	40	118	N.D.[3]
Ammonia	N.D.[3]	N.D.[3]	N.D.[3]	5000

1/Standard method for the examination of water and waste water according to the American Public Health Association; American Water and Waste Water Association, and Water Pollution Control Federation, 13th Edition, 1971.
2/All values in ppm except pH.
3/Not determined.

Table 7. - Product tar analysis and physical properties of dewatered tar from the fluidized-bed gasification of Iowa coal with steam and oxygen at 40 atmospheres

Test No.	210	211
Ultimate analysis of tar,[1] weight percent		
C	83.7	83.8
H_2	6.6	6.4
N_2	0.9	1.0
S	3.2	3.2
O	5.6	5.6
Benzene insolubles, weight percent	0.8	1.1
Viscosity, SSU @ 180° F[2]	132	152
Specific Gravity @ 60/60° F[3]	1.151	1.150
ASTM Distillation, weight percent boiling/°F	48.8/940°	40.2/928°

1/ASTM D271.
2/ASTM D88.
3/ASTM D70.

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